REMARKS

Applicants' attorney thanks the Examiner for his comments. Independent Claim 1 has been amended to state that the low density polyethylene is branched, and is prepared using a high pressure polymerization process. Independent Claim 15 has been amended to state that the ethylene-carbon monoxide copolymer includes a branched low density polyethylene polymer formed using a high pressure polymerization process and a carbon monoxide comonomer. Independent Claim 26 already requires a branched low density polyethylene prepared by a high pressure process, and has not been amended.

The amendments are supported by original Claim 2 (which has been canceled) and the specification at page 5, lines 7-15. As is known in the art, branched low density polyethylene is typically prepared using a high pressure polymerization process. Linear low density polyethylene is prepared using a low pressure polymerization process (similar to the process used to make high density polyethylene, which is also linear). Various dependent claims have been amended for consistency with the independent claims.

a) Claim Rejection Based On Double Patenting

The rejection of Claims 1-37 based on double patenting over Claims 1-37 of U.S. Patent Application 10/762,202 is respectfully traversed. U.S. Patent Application 10/762,202 has now been abandoned via a Notice Of Express Abandonment. This rejection should be withdrawn.

b) Claim Rejection Based On Hirschberger In View Of German et al.

The rejection of Claims 1-4, 6-14, 26 and 30-37 under 35 U.S.C. § 103(a) as obvious over U.S. Patent 4,740,415 ("Hirschberger") in view of U.S. Publication 2004/0072005 ("German et al.") is respectfully traversed. Hirschberger discloses that conventional carriers made of low density polyethylene ("LDPE") are expensive and sometimes crack due to environmental conditions or exposure to grease and machine oil (Col. 2, lines 9-18). Hirschberger further discloses that carriers made from linear low density

polyethylene ("LLDPE") are stiffer, stronger, more resistant to environmental cracking and less expensive (Col. 2, lines 36-45). However, carriers made from LLDPE have various other problems including slippage of LLDPE molecules, relaxation of carrier tension over the containers (causing premature release of containers), necking and insufficient elastic recovery during application, absence of sufficient tension to prevent container release during application, and difficulty in cutting (Col. 2, lines 46-68, Col. 3, lines 1-22).

To alleviate these problems, Hirschberger proposes producing carriers from a blended resin composition including a) LDPE having a density of about 0.920-0.935 grams/cm³ and a melt index of about 0.5-1.0 grams/10 min., and b) LLDPE having a density of about 0.923-0.940 grams/cm³ and a melt index of about 0.75-5.0 grams/10 min. The blend contains about 10-75% by weight LLDPE and about 25-90% by weight LDPE (Col. 3, lines 48-61). Carriers made from the blend provide improved elastic recovery during application, absence of necking, and better establishment and maintenance of tension over the containers (Col. 4, lines 52-68).

Hirschberger establishes a lower density limit of about 0.920 grams/cm³ for the LDPE, and about 0.923 grams/cm³ for the LLDPE, and does not disclose using any polymer having a density below these levels. Hirschberger teaches that a low melt index, a relatively high density and extremely broad molecular weight distribution are required properties for the resins used to make these carriers (Col. 2, lines 31-45).

German et al. discloses blends of metallocene-catalyzed very low density polyethylene ("VLDPE") and LLDPE (Abstract, ¶ 0011). The VLDPE has a density less than 0.916 grams/cm³, suitably 0.900-0.915 grams/cm³. The LLDPE has a density of 0.916-0.940 grams/cm³ (¶¶ 0010, 0011).

According to German et al., the VLDPE is a linear polymer, produced using a low pressure process similar to that used for making LLDPE (¶¶ 0117 and 0132). The VLDPE is made using a gas phase process at pressures of 100 to 1000 psig (¶ 0117). As described in the <u>Handbook Of Plastic Materials And Technology</u> by Irwin S. Rubin (Wiley & Sons, 1990), LLDPE is typically made using a low pressure process at pressures below 2000 psi, often below 1000 psi. (Exh. A, pp. 328-9, 339-40). Branched LDPE, by contrast, is

typically made using a high pressure process at pressures of 15,000-50,000 psi (Exh. A, pp. 318-319). Thus, a fair reading of German et al. is that <u>both</u> polymers in the blend (LLDPE and VLDPE) are linear, and have no long chain branching (¶ 0132). German et al. is concerned with making extruded films with improved properties, but does not address the unique challenges associated with making carriers for containers (¶ 0012).

The combined references do not render Applicants' claims obvious for at least the following reasons. First, it would not have been obvious to modify Hirschberger to substitute a single-site catalyzed ethylene-alpha olefin plastomer having a density between 0.850-0.905 grams/cm³ for the LLDPE disclosed in the reference. As explained above, Hirschberger sets a <u>lower density limit</u> of 0.923 grams/cm³ for the LLDPE, and teaches that the relatively high density is a required property for making suitable carriers. Hirschberger thus <u>teaches away</u> from using polymers having lower density.

Second, Hirschberger and German et al. teach away from each other. As explained above, Hirschberger teaches that a polymer composition containing only linear polyethylene is not suitable for making carriers, and some conventional (i.e., branched) LDPE is necessary. German et al., by contrast, teaches a blend which contains only linear polyethylenes (LLDPE and VLDPE) and does not combine them with branched LDPE having a density of about 0.910-0.950 grams/cm³, prepared using a high pressure process.

Accordingly, there is no suggestion or motivation in the art to disregard the lower density limit mandated by Hirschberger for polymers used in carriers, to permit the inclusion of the substantially lower density polymer required by Applicants' claims. This rejection should be withdrawn.

c) Claim Rejection Based On Hirschberger In View Of German et al. And Balduff

The rejection of Claims 5, 15-25 and 27-29 under 35 U.S.C. § 103(a) as obvious over Hirschberger in view of German et al. and U.S. Patent 4,709,808 ("Balduff et al.") is respectfully traversed. Balduff et al. discloses carriers and other articles formed from three types of polymer blends (Col. 2, line 36 – Col. 3, line 20):

- i) high density polyethylene with ethylene-carbon monoxide polymer,
- ii) linear low density polyethylene with ethylene-carbon monoxide polymer, and
- iii) polypropylene with ethylene-carbon monoxide polymer.

However, there is no suggestion in Balduff et al. to combine an ethylene-carbon monoxide polymer based on branched LDPE, with a single-site catalyzed ethylene-alpha olefin copolymer plastomer having a density of 0.850-0.905 grams/cm³. As explained above, Hirschberger teaches away from using a) linear polymers with densities less than 0.923 grams/cm³ and/or b) compositions of all linear polymers, in carrier materials. German et al. teaches the use of a VLDPE in an all-linear polymer blend, and does not suggest its use in a carrier material. Balduff also does not teach the very low density ethylene-alpha olefin plastomer.

In summary, there is nothing in the prior art which contradicts the teaching in Hirschberger that ethylene polymers used in carrier materials are required to have a density of at least 0.920 grams/cm³ for branched LDPE and at least 0.923 grams/cm³ for linear polymers (i.e., LLDPE). Balduff et al. defines LLDPE as having a broader density range of 0.910-0.940 grams/cm³ (Col. 4, lines 15-25). However, Balduff et al. also presents a broader list of uses (in addition to carriers), some of which may suitably employ a slightly lower density LLDPE (Col.. 2, lines 37-43). Only German et al. discloses a linear polymer having a density below 0.910 grams/cm³, yet does not suggest its use in carrier compositions for containers.

Applicants' claimed invention presents, for the first time, a flexible carrier for containers which employs a single-site catalyzed ethylene-alpha olefin plastomer having a density of about 0.850-0.905 grams/cm³, combined with branched LDPE. This is directly contrary to the teaching of Hirschberger, and is not otherwise suggested by the secondary references. The teaching of Hirschberger reflects the general understanding in the art, that higher density polymers are more suitable.

d) Conclusion

Applicants believe that the claims, as presented, are in condition for allowance. If the Examiner detects any unresolved issues, then Applicants' attorney respectfully requests a telephone interview, and an opportunity to resolve any issues by telephone.

Respectfully submitted,

Manuel fleting

Maxwell J. Petersen

Registration No. 32,772

MJP/mrc

Pauley Petersen & Erickson 2800 West Higgins Road Suite 365 Hoffman Estates, Illinois 60195 TEL (847) 490-1400 FAX (847) 490-1403

Attachments (1) - Exhibit A

Serial No.: 10/762,202 Filing Date: 21 January 2004

· Amendment Exhibit A

HANDBOOK OF PLASTIC MATERIALS AND TECHNOLOGY

Edited by

Irvin I. Rubin Robinson Plastics Corporation





A WILEY-INTERSCIENCE PUBLICATION

John Wiley & Sons, Inc.

NEW YORK / CHICHESTER / BRISBANE / TORONTO / SINGAPORE

Copyright 6 1990 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

Library of Congress Cataloging in Publication Data:

Handbook of plastic materials and technology / edited by Irvin

I. Rubin.

D. cm

Includes bibliographical references.

ISBN 0-471-09634-2

1. Plastics—Handbooks, manuals, etc. J. Rubin, Irvin I., 1919-

TP1130.H35 1990

668.4-dc20

89-48281

CIP

Printed in the United States of America

10 9 8 7 6 5 4 3

ry, 1964.

Polyeth-

28

POLYETHYLENE, LOW DENSITY (LDPE)

Douglas V. Bibee

Senior Development Chemist, Polyethylene Technical Service and Development, The Dow Chemical Co., Freeport, TX 77541

28.1 INTRODUCTION

Low density polyethylene (LDPE) is sometimes called high pressure, low density polyethylene (HPLDPE) to differentiate it from low pressure, low density polyethylene (LPLDPE) or linear low density polyethylene (LLDPE). LDPE commonly is made by polymerizing ethylene at high pressure to form polyethylene molecules

Ethylene gas + High pressure ---- Polyethylene

28.2 CATEGORY

The result (in LDPE) is a highly branched long-chain thermoplastic polymer having density of 57.1-57.7 lb/ft³ (0.915-0.925 g/cm³) and molecular weight up to 4×10^6 . The process also is capable of producing medium density polyethylene (MDPE) up to about 58.3 lb/ft³ (0.935 g/cm³). Figure 28.1 illustrates the differences found among LDPE, LLDPE, and HDPE molecules.

28.3 HISTORY

The introductory section on polyethylenes provides historical information on LDPE. U.S. production of high pressure LDPE was

Year	HPLDPE Billion Pounds	% of Total Plastic
1960	1.2	22
1970	3.7	21
1980	5.7	15
1985	4.9	10

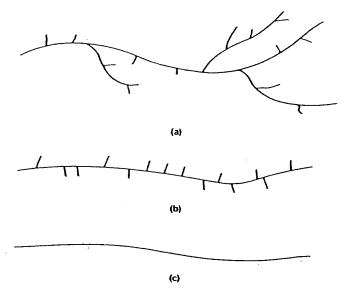


Figure 28.1. Differences in molecules of (a) LDPE, (b) LLDPE, and (c) HDPE.

28.4 POLYMERIZATION

LDPE is produced by the free-radical polymerization of ethylene at high temperature and high pressure. Temperatures vary from 302-572°F (150-300°C); pressures range from 15,000-50,000 psi (103-345 MPa). The polymerization process involves three basic steps: initiation, propagation, and termination.

Initiation requires an initiator, usually a peroxide, that thermally decomposes into free radicals (eq. 28.1), which react with ethylene (eq. 28.2).

Propagation occurs as the chain reaction continues (eq. 28.3).

$$RCH_2CH_2' + CH_2CH_2 - - - - RCH_2CH_2CH_2CH_3CH_3'$$
 (28.3)

Termination of a growing chain occurs when two free-radical groups combine (eq. 28.4), or when a hydrogen radical transfers from one chain to another (eq. 28.5).

$$RCH_{2}CH_{2}' + 'CH_{2}CH_{2}R --------- RCH_{2}CH_{2}CH_{2}CH_{2}R$$
 (28.4) $RCH_{2}CH_{2}' + 'CH_{2}CH_{2}R ---------- RCH_{2}CH_{3} + RCHCH_{2}$ (28.5)

Two commercial methods are used to manufacture LDPE: autoclave and tube. The autoclave process uses a continuous-flow stirred autoclave reactor having an L/D ratio ranging from 2:1 to 20:1. The reactor may be divided by baffles to form a series of well-stirred reaction zones. The autoclave process can produce LDPE resins having a wide range of molecular weight distributions (MWDs).

In the tubular process, the reactor consists of a long tube having L/D ratios greater than 12,000:1. Because there is no mechanical agitation, continuous operation can produce plug flow. Here, the MWD is generally between the extremes achievable by the autoclave.

In both processes, separators downstream from the reactor operate at lower pressures, separating unreacted ehthylene from the polymer. Only 10-30% of the ethylene is converted to polyethylene per pass through the reactor. From the separator, molten polyethylene is extruded through an underwater pelletizer to form pellets. The pellets then are dried and stored in silos until they are loaded into railcars, boxes, or bags.

28.5 DESCRIPTION OF PROPERTIES

The thermal properties of LDPE include a melting range with a peak melting point of 223–234°F (106–112°C). Its relatively low melting point and broad melting range characterize LDPE as a resin that permits fast, forgiving heat-seal operations. The glass-transition temperature T_{ϵ} of LDPE is well below room temperature, accounting for the polymer's soft, flexible nature. The combination of crystalline and amorphous phases in LDPE make determination of T_{ϵ} difficult; however, it can be said that there are significant molecular transitions in LDPE at about -4 and -193°F (-20 and -125°C).

The molten state mechanical properties of LDPE are affected most by molecular weight and MWD. The average molecular weight is routinely measured by the melt index or gel-permeation chromatography. The melt index is a measure of the molten polymer flow rate at a set of conditions specified in ASTM D1238. The high molecular weight results in a low flow rate and low melt index values, so the molecular weight is inversely proportional to the melt index.

In gel-permeation chromatography, a size exclusion technique is used to measure the range of molecular sizes (lengths) present in a polymer, in order to determine the average molecular weight and MWD. The latter is a graphic representation of the relative amounts of each molecular size present in a whole polymer. Figure 28.2 portrays examples of broad and narrow MWD polymers. Although both have the same average molecular weight, the narrow MWD curve indicates that its distribution of molecular sizes is more uniform than that of the broad MWD curve. Such molten state properties of LDPE as melt strength and drawdown are affected by molecular weight and MWD. Melt strength is an indication of how well the molten polymer can support itself, and drawdown is a measure of how thin the molten polymer can be drawn before breaking. Melt strength is increased with increasing molecular weight and broader MWD, while drawdown is increased with lower molecular weight and narrow MWD.

The solid phase mechanical properties of LDPE are influenced most by molecular weight and density and somewhat by MWD (see Table 28.1). The melt index and density often have opposite effects on properties, necessitating compromises in resin selection.

The optical properties of LDPE are affected by molecular weight and density. High molecular weight molecules produce a rough, low gloss surface; higher density polyethylenes contain more or larger crystalline areas that scatter light and cause a hazy appearance. Fabrication conditions have a significant effect on optics.

The environmental properties of LDPE are subject to thermal and ultraviolet degradation. However, additives are available that can extend outdoor service up to several years.

28.6 APPLICATIONS

LDPE film applications include bread bags, shrink wrap, sandwich bags, and garment bags. Substrates extrusion-coated with LDPE are used for milk cartons and many food packaging applications. Blow molded containers of LDPE are used for milk and chemicals. Injection-

HDPE.

nperature and s range from e basic steps:

oses into free

(28.1) (28.2)

(28.3)

не (eq. 28.4),

(28.4)

(28.5)

tube. The L/D ratio ries of wellwide range

POLYETHYLENE LINEAR LOW DENSITY (LLDPE)

Tammy J. Pate

Technical Service and Development, Dow Chemical Co., Freeport, TX 77541

29.1 INTRODUCTION LLDP

Linear low density polyethylene can be described as an ethylene/ α -olefin copolymer having a linear molecular structure. A general representation for the molecule is

where n signifies the number of carbons in the comonomer being used to produce the resin. The comonomers most frequently used commercially are butene, hexene, and octene. LLDPE resins have molecular weights of 10,000-100,000 and varying degrees of crystallinity.

29.2 CATEGORY

LLDPE is a hard, tough, thermoplastic material consisting of a linear backbone with short side-chain branches. The properties of LLDPE in the melt stage and in the finished part are functions of the molecular weight, molecular weight distribution (MWD), and density of the resin. The length and position of the side chains also affect product properties; they are controlled in the production process largely by the comonomer used.

There are many product types: the melt index can range from 0.5-150 g/10 min.; the density from 56.4-58.9 lb/ft³ (0.905-0.945 g/cm³). The resins in the density range of 58.4-58.9 lb/ft³ (0.936-0.945 g/cm³) are often referred to as linear medium density polyethylene resins, while those with densities of 56.4-57.0 lb/ft³ (0.905-0.915 g/cm³) are considered ultra low linear low density polyethylene.

29.3 HISTORY

The introductory section on polyethylenes provides historical information on LLDPE, which has been commercially available for many years. Du Pont Canada developed a process for producing it approximately 20 years ago. Phillips has been producing intermediate-density

LLDPE resins since the early 1960s. However, LLDPE was not a major factor in polyethylene markets until Union Carbide Corp. in 1977 and the Dow Chemical Co. in 1979 announced their commercial activities.

U.S. consumption of LLDPE is increasing rapidly. In 1986, approximately 3.5 billion lb of LLDPE were consumed domestically, representing ahout 20% of the overall polyethylene consumption. The market share of LLDPE is expected to increase to 35% (6.4 billion lb) by 1990.¹²

29.4 POLYMERIZATION

The basic polymerization process requires copolymerizing ethylene and a chosen monomer $(\alpha\text{-olefin})$ using a catalyst. The reactor pressures and temperatures vary depending on the process used. Both the comonomer type and the production process affect the resin's physical properties. Commonly used comonomers are 1-butene, 1-hexene, and 1-octene. Two types of low pressure systems primarily are used to produce LLDPE: the gas-phase fluidized-bed process and the solution processes. LLDPE also can be produced in high pressure, low density polyethylene (LDPE) plants using retrofit technology available (domestically) from Arco and Dow. Table 29.1 lists the North American LLDPE producers, the type of process used, and the announced capacity for each.

The gas-phase fluidized-bed process initially developed by Union Carbide for the production of high density polyethylene (HDPE) has been modified for the production of LLDPE. Gaseous ethylene, hydrogen, a titanium-containing catalyst, and comonomer are continuously fed to a fluidized-bed reactor that operates at a pressure of 304 psi (2.1 MPa) and 176-212°F (80-100°C). Most Union Carbide LLDPE resins currently are produced using I-butene as the comonomer. The company has recently produced LLDPE grades using higher α-olefins as comonomers in their gas-phase process. Polymer product and gas are intermittently discharged from the reactor; the gas is separated from the polymer. The polymer, in powder form, is then air-veyed to storage or to pelletizers.

Du Pont Canada first commercialized LLDPE resins, producing them by the solution process. Dow currently is the only LLDPE producer using a solution process in the United States. In Dow's proprietary process, polymerization occurs in a well-stirred reactor at temperatures of 302-572°F (150-300°C) and at pressures of 435-725 psi (3-5 MPa). Cold ethylene, solvent, a Zeigler-type catalyst, and comonomer are fed continuously to the re-

TABLE 29.1. LLDPE Producers, United States and Canada

Company	Process	Capacity, million It (million kg)
Chevron Dow Chemical, U.S.A. Dow Chemical, Canada DuPont, Canada Eastman Enron Esso, Canada Exxon Mobil Novacor, Canada Union Carbide, U.S.	Solution Solution Solution CDF chemie Gas phase	330 (150) 849 (386) 260 (118) 312 (142) 220 (100)* 249 (113) 299 (136) 649 (295) 374 (170)* 598 (272) 1276 (580)
Jnion Carbide, Canada JSI	Arco	229 (104) 51 (23)

As reported in industry sources.

polyethin 1979

billion lb rethylene illion lb)

nonomer g on the physical wo types ized-bed ure, low ly) from process

the proction of mer are .1 MPa) roduced les using gas are er. The

United actor at 1). Cold the re-

uillion lb

actor. A wide variety of comonomers can be and are used. The Dowlex family of LLDPE resins from Dow are octene copolymers; Sclair resins from Du Pont Canada are butene copolymers. By recycling the solvent removed from the polymer stream, the heat of reaction is removed from the reaction vessel. The molten polymer exits the reactor and is extruded and pelletized. Additives are added at the feed section of the extruder. The molecular weight of the polymer can be controlled by reactor temperature, catalyst composition, and through use of chain terminators. Polymer density is affected by the amount of comonomer fed to the reactor.

Slurry and stirred-bed processes for LLDPE are in various stages of development and in limited use in the United States. These processes are similar to gas-phase and solution processes in that the reactors operate at low pressures and ethylene, comonomer, and catalyst are combined with some type of agitation.

The cost of producing a pound of LLDPE by the several commercial processes is similar because the raw material, ethylene, is the major material component of the manufacturing cost. Also, process yields are said to be comparable. The least expensive basic process is one where the LLDPE is produced as a powder. The cost of pelletizing the powder has been estimated at 9 cents per lb. The manufacturing cost for producing a pound of LLDPE ranges from \$0.26-0.29 per lb, depending on the process, the comonomer used, and the final product form. As of 1988, the range of prices for LLDPE produced in the United States has been \$0.38-0.44 per lb for general-purpose butene copolymers and \$0.42-0.44 per lb for general-purpose octene copolymers.

29.5 DESCRIPTION OF PROPERTIES

LLDPE is an extremely versatile, low-cost polymer adaptable to many fabrication techniques. Tough, chemically inert, and resistant to solvents, acids, and alkalies, LLDPE also possesses good dielectric characteristics and barrier properties. The resin density has a significant effect on the flexibility, permeability, tensile strength, and chemical and heat resistance of LLDPE. Figure 29.1 lists some of the effects of density on various properties of fabricated LLDPE articles.

LLDPE resins can be pigmented and UV stabilized through conventional means. For-

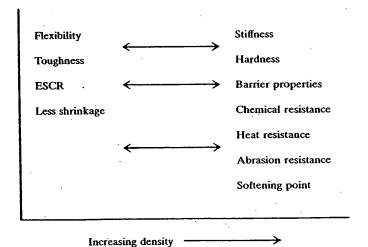


Figure 29.1. The effects of polymer density on fabricated LLDPE articles.

BEST AVAILABLE COPY

30

POLYETHYLENE, HIGH DENSITY (HDPE)

Robert J. Beam

Data Management Supervisor, Dow Chemical U.S.A., 2040 Willard H. Dow Center, Midland, MI 48674

30.1 INTRODUCTION

For normal molecular weight polyethylenes (melt index >0.5), the density of homopolymer HDPE is fixed at 59.9-60.2 lb/ft³ (0.960 to 0.965 g/cm³), depending on the manufacturing process. However, HDPE spans the density range of 58.7-60.3 lb/ft³ (0.941 to 0.967 g/cm³) by the use of copolymers that add side-chain branches and thus reduce the density.

The density of HDPE is controlled in the manufacturing process by the amount of comonomer added to the reactor. Typical comonomers used with ethylene in HDPE are propylene, butene, hexene, and octene. As the molecular weight of polyethylene increases, the longer polymer chains do not crystallize as readily and the lower amount of crystallinity further reduces the density of a HDPE homopolymer (melt index <0.5).

30.2 CATEGORY

HDPE is a partially crystalline, partially amorphous thermoplastic material. The degree of crystallinity depends on the molecular weight, the amount of comonomer present, and the heat treatment given. The crystallinity of a given HDPE resin can be varied over a wide range by the rate of cooling from the molten state; slower cooling rates favor crystalline growth. The range of crystallinity for HDPE is normally 50–80%. A density value normally quoted on data sheets for HDPE is determined by a compression molded sheet that has been cooled at the rate of 27°F (15°C) per minute. ¹⁻³ Most commercial fabrication processes cool from the melt at much faster rates; as a result, an article fabricated from HDPE rarely reaches the density quoted on a data sheet. Because the amount of crystallinity in HDPE is variable, HDPE can be considered as an amorphous polymer having a variable amount of crystalline filler.

30.3 HISTORY

The introductory section on polyethylenes provides historical information on HDPE.

30.4 POLYMERIZATION

HDPE is manufactured by a low pressure process; by comparison, low density polyethylene (LDPE) is manufactured by a high pressure process. The pressure used in manufacturing

Proceedings),

ocess," SPE

kron, Ohio,

iere Are We

PE," TAPPI

on," TAPPI

APPI Paper

PE RETEC

PE RETEC

ıds," *TAPPI*

LDPE Film

Film," SPE

dings), Ak-

roceedings),

roceedings),

ssing Blown

Ohio, Sept.

C (Proceed-

TEC (Pro-

Feb. 1982).

of Primary

'E RETEC

? (Proceed-

Sept. 1982,

oceedings),

HDPE is below 2000 psi (14 MPa); in many cases, it is below 1000 psi (7 MPa). [In manufacturing LDPE, pressures commonly exceed 10,000 psi (70 MPa).]

There are three major commercial processes used for polymerization of HDPE: solution, slurry, and gas-phase processes. The catalysts used in the manufacture of HDPE are usually either a transition metal oxide type or a Ziegler/Natta type. It is important to note that the performance of HDPE resins having identical melt indexes, densities, and molecular weight distributions (MWDs) can vary if the resins are produced by different processes. These differences normally are seen only in critical applications having very narrow processing windows. For most applications, HDPE resins selected from more than one supplier will perform adequately.

perform adequately, even if the resins are made by different processes.

As mentioned, along with melt index and density, MWD is a distinguishing property of HDPE. As HDPE is polymerized, polymer molecules of many different lengths (molecular weights) are produced. If an HDPE resin has a narrow range of molecule lengths, it is said to have a narrow MWD. Conversely, an HDPE having a broad range of molecule lengths is said to have a broad MWD. The MWD is a plot of molecular weight versus the number or frequency of a given molecular weight. As the MWD of an HDPE is broadened, the processibility and melt strength increase, while impact strength, low-temperature toughness, and warpage resistance decrease. The MWD of HDPE is largely controlled by the type of catalyst used in polymerization and by the type of manufacturing process employed.

30.5 DESCRIPTION OF PROPERTIES

In HDPE, the properties of tensile yield strength, stiffness, creep resistance, impermeability, abrasion resistance, mold shrinkage, and hardness increase with increasing density. On the other hand impact strength, flexibility, and environmental stress crack resistance (ESCR) increase with decreasing density.

As the average molecular weight of HDPE increases, the polymer's molten flow decreases. The standard test for measuring the molten flow of HDPE is called the melt index. Melt index is inversely proprotional to the average molecular weight. The properties of ESCR, impact strength, tensile strength, elongation, melt strength, and die swell improve with decreasing melt index (and with increasing average molecular weight). The properties of processibility, melt drawdown, and optics decrease with decreasing melt index. As the average molecular weight of HDPE increases, there is more shrinkage and warpage present in the molded parts.

These brief comments on melt index and density indicate that it is not possible to maximize all of the properties of HDPE in a single resin. Therefore, compromises are necessary in designing any HDPE resin. For that reason, most manufacturers of HDPE offer many different HDPE resin grades in their product mix. Selection of an HDPE resin for a given application involves careful evaluation of the application requirements, in order to select

the HDPE resin that most closely satisfies the most important requirements.

The glass-transition temperature T_s of polyethylene is well below room temperature. This gives polyethylene its more rubbery nature (compared to a polymer such as polystyrene which has a glass-transition point above room temperature). The rubbery nature of HDPE also limits its service temperature compared to that of a polymer having a T_s above room temperature. The T_s for HDPE has been assigned several different values by different measuring techniques and is the subject of much controversey. There are three temperature ranges commonly assigned as the glass-transition point for polyethylene: -207 to -171° F (-133 to -113° C), -126 to -99° F (-88 to -73° C), and -45 to 9° F (-43 to -13° C).

Because HDPE is rubbery, its creep modulus is more important than, for example, its flexural modulus in determining the in-service strength of a part fabricated from it. In designing an HDPE part that is intended to bear a load for an extended period of time (greater than one hour), flexural or tensile modulus cannot safely be used to calculate the strength of the fabricated part. Instead, the designer should refer to creep data and select